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## (54) Use of polyaminoamide resins as adhesion promoters of PVC plastisols

Verwendung von Polyaminoamideharzen als Adhäsionspromotoren in PVC-Plastisolen

Utilisation de résines de polyaminoamide comme promoteurs d'adhésion pour des plastisols de P.V.C.

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## Description

**[0001]** It is known that plastisols are essentially constituted by a liquid dispersion of a polymer or copolymer of vinyl chloride in the form of a powder inside a plastifier, in which the polymer must not be soluble to an appreciable extent at room temperature.

**[0002]** When these plastisols undergo the action of heat, a dissolution of the polymer in the plastifier is accomplished, with the formation of a more or less elastic homogeneous mass.

**[0003]** Plastisols are mostly used as insulating and sound-proofing coatings, e.g., in the automotive industry, by means of the application to different types of metal surfaces, towards which they exhibit however a very poor adhesion.

**[0004]** It has been known for a long time from the common experience that such an adhesion is increased if to the plastisol polyamidic resins, which are homogeneously dispersible therein, are added.

**[0005]** According to the known art, suitable to that purpose have resulted the polyaminoamide and polyaminoamidoimidazoline resins, which are prepared by means of the condensation of aliphatic polyamines with polycarboxylic acids obtained from the polymerization of the unsaturated fatty acids.

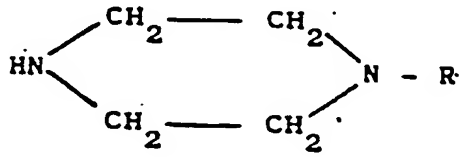
**[0006]** Such polyaminoamide and polyaminoamidoimidazoline resins, as prepared with aliphatic amines, although they fulfil the function of increasing, to a different extent according to their composition, the adhesion of plastisols to the surfaces to be coated, show the drawback of imparting to the end coating a more or less intense brown colour, which is developed during the thermal treatment.

**[0007]** By means of the present invention is demonstrated on an experimental basis that, if instead of the aliphatic polyamines, piperazine and/or some derivatives thereof, such as aminoethylpiperazine is used, by following particular formulation criteria which shall be disclosed hereinunder, the polyaminoamide resins which are obtained, besides to excellently fulfilling the function of acting as adhesion promoter for the plastisol, do not give rise to the drawback of altering the colour of the end coating, as it has hereinabove described.

**[0008]** From FR-A-2141 878 polyaminoamide resins made from polymeric fatty acids and piperazine as well as their use as hot melt adhesives for vinylic polymers are known.

**[0009]** The object of the present invention are therefore the use of adhesion promoters for plastisols of polyvinyl polymers or copolymers, characterized in that they are constituted by polyaminoamide resins obtained by means of the condensation of:

- 1 equivalent of polycarboxylic acids, obtained by means of the polymerisation of usaturated fatty acids, of composition comprised within the following ranges: 0 - 20%, preferred 0 - 2% monomers, 10 - 80%, preferred 10 - 50% dimers, 18 - 90%, preferred 50 - 90% trimers, with
- from 1.0 to 2.2 equivalents of an heterocyclic amine of the general formula



wherein R can be H or an alkylamino group -R'-$NH_2$, wherein R' is a saturated alifatic chain.

**[0010]** Among the hereinabove disclosed cycloaliphatic amines, piperazine and aminoethylpiperazine are preferred.

**[0011]** The condensation process in the preparation of the resins consists in heating the polycarboxylic acids and the amines as described together with each other, at temperatures not lower than 120°C and preferably comprised within the range of from 150 to 230° C for a time period long enough to eliminate all condensation water, and then applying vacuum to complete the reaction, and removing the amine which is remained unchanged.

**[0012]** According to the invention the polyaminoamide resins are used as adhesion promoters for plastisols both as such and in solution.

**[0013]** Both the concentration of the solution, and the type of solvent may be varied according to the viscosity of the resin and to its solubility.

**[0014]** The solvents suitable to that purpose can be selected within a broad range of organic products, such as hydrocarbons, the chloro- and nitro-derivatives thereof, alcohols, polyols, esters, ketones, amines and amides.

**[0015]** To the purpose of better describing the resins according to the invention, some examples of preparation thereof, as numbered from 4 to 11, which are in no way to be considered as limitative, are reported hereinunder.

**[0016]** Such examples are preceded by examples, as numbered from 1 to 3, relating to the preparation of resins according to the known art; these latter are reported to comparison purposes with the resins according to the invention, as it shall be disclosed in the following.

Example 1 (Comparison)

Polyaminoamide resin from polymerized fatty acids and aliphatic amine

**[0017]** 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from unsaturated fatty acids of 18 carbon atoms, having the following composition 10% monomers, 74% dimers, 16% trimers) are heated, while being stirred, with 138.7 parts by weight (1.9 equivalents) of triethylenetetramine, until they reach the temperature of 210°C, and are then held at such a temperature, the reaction water being distilled off, for 1 hour, vacuum is then applied 90 - 95 mbar (70 - 72 mmHg), the temperature of 210°C being maintained for a further hour, after which the heating is disconnected, and the obtained resin , having an amine number (mg of KOH/g, as determined by potentiometric titration with perchloric acid) of from 340 to 360, is discharged.

Example 2 ( Comparison)

Polyaminoamide resin from polymerized fatty acids and aliphatic polyamine

**[0018]** 285 Parts by weight (1 equivalent) of polymerised fatty acids (as obtained from unsaturated $C_{18}$ fatty acids, having the following composition: 4% monomers, 61% dimers, 35% trimers) are heated, under stirring, with 156.95 parts by weight (2.15 equivalents) of triethylenetetramine under the same conditions, and within the same time periods as disclosed in Example 1.

**[0019]** The obtained resin has an amine number comprised within the range of from 380 to 410.

Example 3 (Comparison)

Polyaminoamidoimidazoline resin from polymerized fatty acids and aliphatic polyamine

**[0020]** The same amounts of polymerized fatty acids and of triethylenetetramine as disclosed in Example 2 are heated, while being stirred, until they reach the temperature of 230°C, and are kept at said temperature, the reaction water being distilled off, for 1 hour, vacuum 90 - 95 mbar (70 - 72 mmHg) is then applied, the temperature being maintained for the time necessary for the formation inside the resin of at least 80% of imidazoline (as determined by I.R. spectroscopy), after which the heating is disconnected and the obtained resin, having an amine number comprised within the range of from 380 to 480, is discharged.

Example 4

Polyaminoamide resin from polymerized fatty acids and piperazine

**[0021]** 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from $C_{18}$ unsaturated fatty acids, having the following composition: 15% dimers, 85% trimers) are heated under stirring with 86 parts by weight (2 equivalents) of piperazine, until they reach the temperature of 180°C, and are kept at such a temperature until the maximum neutralization of acidity ( about 5 mg of KOH/g) is obtained, which takes place within a time of about 4 hours.

**[0022]** The heating is then disconnected, and the resin, having an amine number comprised within the range of from 140 to 150, is unloaded.

Example 5

Polyaminoamide resin from polymerized fatty acids and piperazine

**[0023]** The same components, in the same ratio as shown in Example 4, are heated under stirring, until they reach the temperature of 180°C, and are held at such a temperature for 2 hours, vacuum is then applied 90-95 mbar (70 - 72 mmHg), with the temperature being maintained for a further hour.

**[0024]** The heating is then disconnected, and the resin, having an amine number of from 80 to 100, is discharged.

Example 6

[0025]

Polyaminoamidic resin from polymerized fatty acids and piperazine

[0026] 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from $C_{18}$ unsaturated fatty acids having the following composition: 20% monomers, 12% dimers, 68% trimers) are heated while being stirred with 86 parts by weight (2 equivalents) of piperazine, until the temperature of 180°C is reached, the process being then continued under the same conditions as disclosed in Example 5.

[0027] The obtained resin has an amine number comprised within the range of from 80 to 100.

Example 7

Polyaminoamide resin from polymerized fatty acids and piperazine.

[0028] 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from $C_{18}$ unsaturated fatty acids, having the following composition: 2% monomers, 80% dimers, 18% trimers) are heated, under stirring, with 86 parts by weight (2 equivalents) of piperazine, until they reach the temperature of 180°C, the process being then continued under the same conditions as disclosed in Example 5.

[0029] The obtained resin has an amine number of from 80 to 100.

Example 8

Polyaminoamide resin from polymerized fatty acids and piperazine

[0030] 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from $C_{18}$ unsaturated fatty acids and having the following composition: 1% monomers, 47% dimers, 52% trimers) are heated, while being stirred, with 80 parts by weight of piperazine, until the temperature of 180°C is reached, by operating under the same conditions as disclosed in Example 5.

[0031] The resin obtained has an amine number within the range of from 80 to 90.

Example 9

Polyaminoamide resin from polymerized fatty acids and piperazine.

[0032] 285 Parts by weight (1 equivalent) of polymerized fatty acids (as obtained from $C_{18}$ unsaturated fatty acids having the following composition: 2% monomers, 80% dimers, 18% trimers) are heated under stirring with 51.6 parts by weight (1.2 equivalents) of piperazine, until they reach the temperature of 180°C, the process being carried out under the same conditions as of Example 5.

[0033] The obtained resin has an amine number of from 50 to 60.

Example 10

Polyaminoamide resin from polymerized fatty acids and aminoethylpiperazine

[0034] 285 Parts by weight (1 equivalent) of polymerized fatty acids (obtained from unsaturated fatty acids and having the following composition: 15% dimers, 85% trimers) are heated, while being stirred, with 129 parts by weight (2 equivalents) of aminoethylpiperazine, until the temperature of 180°C is reached, the process being carried out under the same conditions as disclosed in Example 5. The obtained resin has an amine number of from 260 to 280.

Example 11

Polyaminoamide resin from polymerized fatty acids and aminoethylpiperazine

[0035] 285 Parts by weight (1 equivalent) of polymerized fatty acids as disclosed in Example 10 are heated, while being stirred, with 100 parts by weight (1.55 equivalents) of aminoethylpiperazine, until they reach the temperature of 180°C, the process being carried out under the same conditions as disclosed in Example 5.

**[0036]** The resin obtained has an amine number comprised within the range of from 195 to 205.

**[0037]** The products obtained according to the examples described have been submitted to an application test, as adhesion promoters, on a plastisol of the following % composition:

| | |
|---|---|
| Polyvinyl chloride | 22 |
| Dioctyl phtalate | 28 |
| Calcium carbonate | 50 |

to which the 1% of adhesion promoter has then been added. The samples of plastisols with each one of the adhesion promoters, as obtained according to the examples described, have been compared as for the adhesion value, and for the colour stability, with 30-minute baking, at different temperatures.

**[0038]** The adhesion tests have been carried out by submitting to the tensile shear strength test two steel specimens of mm 100 x 25 in size, surface-roughened by means of emery cloth, bonded by means of a layer of 1 mm in thickness of the plastisol being tested, for an area of 500 $mm^2$ and baked for 30 minutes at the predetermined temperature.

**[0039]** The adhesion strength, obtained from the average of 5 tests, is expressed as $kg/cm^2$ and the colour stability value is expressed by means of a visual evaluation, as indicated with U = unaltered; Y = discoloured to a yellow colour, followed by the + symbol repeated from once to three times, according to the intensity of the yellow colour obtained.

**[0040]** The results obtained from such tests are shown in the following Table:

| Baking Temperature | 120°C | | 140°C | | 160°C | |
|---|---|---|---|---|---|---|
| | Adhesion | Colour | Adhesion | Colour | Adhesion | Colour |
| Ex. Nr 1 | 4.4 | Y | 5.8 | Y+ | 7.4 | Y++ |
| Ex. Nr 2 | 4.9 | Y | 6.7 | Y+ | 8.0 | Y++ |
| Ex. Nr 3 | 5.4 | Y | 6.8 | Y+ | 8.9 | Y++ |
| Ex. Nr 4 | 4.1 | U | 4.8 | U | 7.3 | U |
| Ex. Nr 5 | 6.8 | U | 7.6 | U | 9.0 | U |
| Ex. Nr 6 | 3.9 | U | 4.4 | U | 7.0 | U |
| Ex. Nr 7 | 2.6 | U | 3.0 | U | 5.8 | U |
| Ex. Nr 8 | 5.4 | U | 6.4 | U | 8.2 | U |
| Ex. Nr 9 | 4.5 | U | 6.8 | U | 7.0 | U |
| Ex. Nr 10 | 4.2 | U | 4.9 | U | 7.4 | U-Y |
| Ex. Nr 11 | 6.5 | U | 7.7 | U | 9.5 | Y |

**[0041]** As it is shown by such results, with all the products according to the invention (adhesion promoters of the examples from 4 to 11), plastisols are obtained whose colour remains unchanged at all tested temperatures.

**[0042]** Tests carried out at temperatures higher than indicated in the Table (230°C) have shown that, whilst the plastisols containing the adhesion promoters as of Examples from 1 to 3 become completely black, those containing the adhesion promoters according to the invention are discoloured to a yellow colour to a not greater extent than plastisol free from adhesion promoter.

**[0043]** Such a property occurs also in the case of the so-called "low temperature" plastisols, which, due to their particularly high content in polyvinyl acetate are particularly sensible to the discolouring action of the polyaminoamide adhesion promoters of the type as of Examples from 1 to 3; if to such plastisols adhesion promoters according to the invention are added, they can be treated at higher temperatures than those prescribed, without any colour alterations.

**[0044]** As for the adhesion, the data contained in the Table show that the adhesion promoters according to the invention, if obtained by means of suitable process and formulation (Examples Nos. 5 and 11) can yield better results than those to be obtained with known polyaminoamide adhesion promoters of commerce (Examples from 1 to 3).

## Claims

1. Use of polyaminoamide resins as adhesion promoters for plastisols of polymers or copolymers of polyvinyl chloride, characterized in that they are constituted by polyaminoamide resins as obtained by means of the condensation of:

   - 1 equivalent of polycarboxylic acids, as obtained by means of the polymerization of unsaturated fatty acids, whose composition is comprised within the following range:

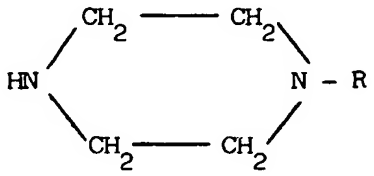
     0 - 20% monomers

     10- 80% dimers

     18- 90% trimers

   with

   - from 1.0 to 2.2 equivalents of an heterocyclic amine of the general formula



   wherein R can be H or an alkylamino group -R'-$NH_2$, wherein R' is a saturated aliphatic chain.

2. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 1, characterized in that said unsaturated fatty acids have the following composition range: 0-2% monomers, 10-50% dimers, 50-90% trimers.

3. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 1, characterized in that the polycarboxylic acids used are obtained from unsaturated acids of 18 carbon atoms and have the following composition: 15% dimers, 85% trimers.

4. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 1, characterized in that the heterocyclic amine used is piperazine.

5. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 4, characterized in that the equivalent ratio of polycarboxylic acid to amine is of 1 to 2.

6. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 1, characterized in taht the heterocyclic amine is aminoethylpiperazine.

7. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 6, characterized in that the equivalent ratio of polycarboxylic acid to the heterocyclic amine is of 1 to 1.2.

8. Use of polyaminoamide resins as adhesion promoters for plastisols according to claim 1, characterized in that they are dissolved in an organic solvent.

9. Plastisols of polymers or copolymers of polyvinyl chloride characterized in that they contain as the adhesion promoter a polyaminoamide resins, as defined in any one of the preceding claims.

## Patentansprüche

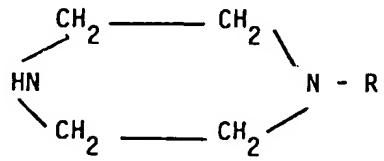
1. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole von Polymeren oder Copolymeren von Polyvinylchlorid, dadurch gekennzeichnet, dass sie von Polyaminoamidharzen gebildet sind, die durch die

Kondensation von:

- 1 Aequivalent von polycarbocyclischen Saeuren, erhalten durch Polymerisation von ungesaettigten Fettsaeuren, die den folgenden Zusammensetzungsbereich haben:

  0 - 20 % Monomere
  10 - 80% Dimere
  18 - 90% Trimere

  mit
- von 1,0 bis 2,2 Aequivalenten eines heterocyclischen Amins der allgemeinen Formel



worin R Wasserstoff oder eine Alkylaminogruppe -R' -$NH_2$ bedeutet, wobei R' eine gesaettigte aliphatische Kette bedeutet, erhalten wurden.

2. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 1, dadurch gekennzeichnet, dass die ungesaettigten Fettsaeuren den folgenden Zusammensetzungsbereich haben: 0-2% Monomere, 10-50% Dimere, 50-90% Trimere.

3. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 1, dadurch gekennzeichnet, dass die verwendeten polycarbocyclischen Saeuren aus ungesaettigten Saeuren mit 18 Kohlenstoffatomen erhalten sind und die folgende Zusammensetzung haben: 15% Dimere, 85% Trimere.

4. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 1, dadurch gekennzeichnet, dass das verwendete heterocyclische Amin Piperazin ist.

5. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 4, dadurch gekennzeichnet, dass das Aequivalentverhaeltnis von polycarbocyclischer Saeure zu Amin 1 bis 2 betraegt.

6. Die Verwendung von Polyaminoharzen als Haftverbesser fuer Plastisole nach Anspruch 1, dadurch gekennzeichnet, dass das heterocyclische Amin Aminoaethylpiperazin ist.

7. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 6, dadurch gekennzeichnet, dass das Aequivalentverhaeltnis von polycarbocyclischer Saeure zu heterocyclischem Amin 1 bis 1.2 betraegt.

8. Die Verwendung von Polyaminoamidharzen als Haftverbesserer fuer Plastisole nach Anspruch 1, dadurch gekennzeichnet, dass sie in einem organischen Loesungsmittel geloest sind.

9. Plastisole von Polymeren oder Copolymeren von Polyvinylchlorid, dadurch gekennzeichnet, dass sie als Haftverbesserer ein Polyaminoamidharz, wie in einem der vorstehenden Ansprueche definiert, enthalten.

**Revendications**

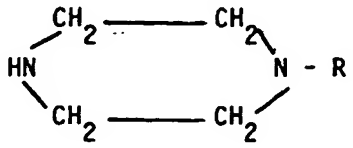
1. Utilisation de résines de polyaminoamide en tant que promoteurs de adhésion pour plastisols de polymères ou copolymères de poly(chlorure de vinyle), caracterisés en ce qu'ils sont constitués par des résines de polyaminoamide obtenu par la condensation de:

   - 1 équivalent d'acides polycarboxyliques obtenus par polymérisation d'acides gras insaturés, qui comportent dans leur formulation:

0 - 20 % de monomères
10- 80 % de dimères
18- 90 % de trimères

avec

- 1.0 à 2.2 équivalents d'une amine hétérocyclique de formule générale



où R peut être H ou un groupe alkylamino -R' -$NH_2$ dans lequel R' est une chaîne aliphatique saturée.

2. Utilisation de résines de polyaminoamide en tant que promoteurs de adhésion pour plastisols selon la revendication 1, caractérisée en ce que lesdits acides gras insaturés comportent dans leur formulation: 0-2% de monomères, 10-50% de dimères, 50-90% de trimères.

3. Utilisation de résines de polyaminoamide en tant que promoteurs de adhésion pour plastisols selon la revendication 1, caractérisée en ce que les acides polycarboxyliques utilisés ont eté obtenus d'acides insaturés ayant 18 atomes de carbone et comportent dans leur formulation : 15% de dimères , 85% de trimères.

4. Utilisation de résines de polyaminoamide en tant que prometeurs de adhésion pou plastisols selon la revendication 1, caractérisée en ce que l'amine hétérocyclique est la pipérazine.

5. Utilisation de résines de polyaminoamide en tant que promoteurs de adhésion pour plastisols selon la revendication 4, caractérisée en ce que le rapport des équivalents acide polycarboxylique/amine est de 1 à 2.

6. Utilisation de résines de plyaminoamide en tant que promoteurs pour plastisols selon la revendication 1, caractérisée en ce que l'amine hétérocyclique est l'aminoéthylpipérazine.

7. Utilisation de résines de polyaminoamide en tant que promoteurs d'adhésion pour plastisols selon la revendication 6, caractérisée en ce que le rapport des équivalents acide polycarboxylique/amine est de 1 à 1.2.

8. Utilisation de résines de polyaminoamide en tant que promoteurs d'adhésion pur plastisols selon la revendication 1, caractérisée en ce que lesdits résines de polyaminoamide sont dissoutes dans un solvant organique.

9. Plastisols de polymères ou copolymères de poly(chlorure de vinyle), caractérisés en ce qu'ils contiennent en tant que promoteur de adhésion une résine de polyaminoamide telle que définie dans l'une quelconque des revendications précédentes.